Fibre-reinforced shaped article and process for its production.

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The shaped article of hydraulic binder contains, as reinforcing fibres, birch pulp fibres alone or together with other fibre materials and, if appropriate, fillers. The shaped article is especially suitable as a building component, for example as a building panel, and shows particularly good material properties.

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(corresponding to EP 0287962 B1)

Title: A shaped article formed by a hydraulic binder and fibers, as well as optionally by fillers, coloring agents and other additives.

DESCRIPTION

The invention relates to a shaped article formed by a hydraulic binder and fibers, as well as optionally by fillers, coloring agents and other additives.

The substitution of the asbestos fibrocement products by other construction elements of the same type, but without asbestos fibers, has gained increasing importance in the construction during the last years. On the one hand, it is known that when the manufacture and elaboration of the asbestos fibrocement are not sufficiently careful, asbestos dust arises, which is particularly dangerous for the health. On the other hand, the reduction of the asbestos natural sources forces to search for other alternative products which can be utilized without problems in the present field of application of the asbestos fibrocement.

For this purpose, the substitution of the asbestos with other natural or synthetic fibers, or mixtures thereof, has been already recommended for the manufacture of inorganic fiber-reinforced and hydraulically bound shaped articles.

It is also known the utilization of the cellulose fibers instead of the asbestos, taken along or in combination with other synthetic organic fibers, in order to reinforce cement or concrete objects.

However, already known materials of this type always have inconveniencies and technical disadvantages in their manufacture and utilization, especially in comparison with the asbestos fibrocement. They are too expensive to produce, particularly due to the elaboration of the raw materials or mixtures thereof, and, on the other hand, their resistance to bending and impacts is reduced, so that they do not satisfy use requirements, for example, the requirements established by the construction standards.

(DE-C 24 63 044) and (DE-C 29 40 623) have proposed the use of hemp and eucalyptus fibers, respectively, as new fibrous materials for reinforcing the cement. However, these materials have significantly lower resistance than asbestos fibrocement, especially in the non pressed products. A great disadvantage of this type of fibrocement is that it has a very low impact resistance and a very low breakage resistance. Furthermore, due to their totally insufficient aptitude for being shaped and/or plasticity aptitude, it is not possible to manufacture with this type of mixtures any profile class, such as, for example, undulating plates. Moreover, according to the cited patent documents, it is indispensable to use decorated cellulose, which together with the high costs of the raw material has a disadvantage of more reduced duration. Also, the other recommended types of cellulose, such as, for example, cellulose or eucalyptus fiber, can be only used in the limited forms and are not the national raw materials.

Therefore, the known state of the art does not give any satisfactory solution for manufacturing fiber-reinforced asbestos-free inorganic products, which have good

properties and can be used instead of the asbestos fibrocement and which also can be economically produced.

This problem is solved according to the invention by means of shaped articles and reinforcing fibers added thereto, such as bleached or unbleached birch cellulose fibers, taken along or in combination with other cellulose fibers.

Owing to the invention, it is possible the economical manufacture of a fiber-reinforced inorganic binding product which does not have the aforementioned disadvantages.

The shaped articles are characterized by their good bending and impact resistances, as well as a good breakage resistance, so that they can be widely utilized for substituting the asbestos fibrocement articles in the construction.

It is surprising for the expert in the art that the bleached birch cellulose, and preferably unbleached, is precisely adequate for the use as reinforcing fiber for the products manufactured with hydraulic binders. It should be pointed out the fact that the use of birch cellulose, according to the invention, provides an unexpectedly good combination of technical characteristics for bleached manufacture and use. On the contrary to the eucalyptus cellulose, a good behavior for water removal and good aptitude for shaping the plates, allows that the undulated plates, pressed o non pressed, manufactured with birch cellulose mixtures, in addition to a high bending resistance, are characterized by high breakage, impact and frost resistance.

In this context, the steam-hardened objects can be also manufactured with birch cellulose, better than with other known cellulose types, which when being bound with each

other contain quartz dust with calcium hydroxide, and which have to be used as undulated plates, and also particularly as the construction elements that should have special incombustible capacities, for example, for covering steel joists or for incombustible coverings of ventilation pipes.

According to the invention, the shaped articles are manufactured with bleached or unbleached birch cellulose, taken along or in combination with other natural and/or synthetic fibers, among which mainly are mixtures of birch cellulose with palm, linen, abaca, fir tree, pine and/or sisal cellulose, or hard cellulose fibers.

According to the invention, among many variants of possible execution forms there are some examples indicated below.

Example 1

About 2500 parts by weight of water are put into a paste disintegrator and 90 parts by weight of unbleached material (16 SR degrees) are added in a flake form. After the preparation during approximately 30 minutes, spinning at 800 rpm, the suspension is concentrated and mixed in a mixing apparatus with 1000 parts by weight of Portland cement.

The aqueous fibrous and cement suspension is moved into a mixing barrel and therefrom – in this case with an addition of polyelectrolytes (0.001 to 0.25 % by weight of polyacrylamide, with respect to the utilized cement) – it is moved directly into a molding machine, wherein by means of the fiber deposition and drying-up processes, analogous to the Hatschek or Magnani processes, the suspension is shaped forming a tube or a plate.

A bending and breakage resistance of the shaped article is determined by 28 days of open air storage.

(The data concerning the bending and breakage resistance are found in the table 1 of an appendix).

Example 2

The birch cellulose is suspended in water as in the previous case.

600 parts by weight of Portland cement and 400 parts by weight of quartz dust (fineness of approximately 5000 Blaine) are mixed with the concentrated cellulose suspension and the mixture is being elaborated in the form of plates in the direct molding machine.

The shaped articles are stored during three days in the open air, then they are heated up in an autoclave to 6 bar and 338 K during 16 hours and, after 3 more days of the open air storage their resistance is determined as in the example 1.

(The data concerning the bending and breakage resistance are found in the table 2 of the appendix).

Example 3

From 20 to 80 parts by weight of birch cellulose and 70 to 10 parts by weight of linen and/or sisal cellulose are dissolved in a paste disintegrator, in the same way as in the previous examples and – alternatively – a hardened in the open air shaped article is formed utilizing Portland cement as binder, as in the example 1, a steam-hardened shaped article is formed utilizing Portland cement and quartz as binders.

The resistances are determined as in the example 1, after 28 days, or after 3 days of the open air storage of the shaped article.

(The data concerning the bending and breakage resistance are found in the table 3 of the appendix).

Example 4

A cellulose suspension corresponding to the previous examples is elaborated in a mixing device with approximately 800 parts by weight of Portland cement, or a mixture of Portland cement and quartz, according to the example 2, as well as with 300 parts by weight of perlite and/or mica and/or vermiculite, and the shaped article is formed in a direct molding machine.

A bending and breakage resistance is determined after 28 days of the open air hardening or, alternatively, of the steam-hardening, as in the example 1.

(The data concerning the bending and breakage resistance are found in the table 4 of appendix).

Example 5

A shaped article is formed in the form of plate with a cellulose suspension corresponding to the previous examples of mixtures, with 550 parts by weight of fine quartz dust (Blaine > 5000), as well as with 300 to 450 parts by weight of calcium hydroxide.

The shaped article is treated in an autoclave with water steam at 16 bar during approximately 8 hours, or with water steam at 8 bar during 20 hours, and, then it is stored

in the open air during 3 days. After that, the resistances are determined as in the previous examples.

(The data concerning the bending and breakage resistance are found in the table 5 of appendix).

Example 6

According to examples 1 to 5, water is added in a mixing apparatus to cellulose and binder suspension until the content of solid matter becomes from 4 to 10 % by weight and, then a shaped article is formed, in the form of a tube or a plate, by means of the known Hatschek process.

Simultaneously to the operation tests carried out with mixtures according to the invention, other shaped articles are formed with the known cellulose and binder mixtures, for example, according to the formula of DE-C-29 40 623, and the same resistance tests are carried out with these samples. (See the measurement data in the table 6).

The results of material tests shown in the table 6a (see appendix) reflect a selection, as an example, of the numerous series of tests of the previous examples. It can be deduced therefrom that according to the invention, the recommended use of birch cellulose and/or mixtures of birch cellulose with other celluloses or hard cellulose fibers, mainly with sisal fibers, allows manufacturing asbestos-free shaped articles comprising hydraulic binder and fibers, which characteristics and properties are superior to the previously known proposals.

The improved profitability is added thereto, owing to the use of national or European and, therefore, more economical and a lot easier to obtain, including in the future, raw materials.

Example 7

The mixtures indicated below were manufactured according to examples 1-5 with addition of water into a mixing apparatus until the content of solid matter became from 4 to 10 % by weight, and undulated plates of perlite 7 of 6 mm of thickness were manufactured with those mixtures in a Hatschek´s machine. The recently done plates were left to get harden during 3 days, located between two lubricated undulated plates. After that, the plates were treated in an autoclave during 16 hours at 6 bar. Some variants of pressed (30 minutes at 180 bar) and non pressed plates were manufactured with the mixture 1.

With the mixtures number 1-4 of the table 7 (see appendix), it was observed that the aptitude of the mixtures number 1-3 to become undulated was completely satisfactory. In the mixture number 4 numerous cracks have appeared during the undulating process. The samples number 2 and 3 were shown as optimums for undulating, offering satisfactory results, including when the curvature radius was little.

The properties of thus manufactured undulated plates have been compiled in the table 8 (see appendix).

CLAIMS

1. A shaped article usable as construction element, comprising a hydraulic binder and natural and/or synthetic inorganic and/or organic fibrous materials as well as optionally filler materials, characterized in that the reinforcing fibers comprise bleached or unbleached birch cellulose fibers, taken along or in combination with other fibrous materials.

2. A shaped article according to claim 1, characterized in that the part of reinforcing fibers comprises 1 to 15 % by weight of the mixture of fibers, binder and optionally fillers and coloring agents as well as other additives.

3. A shaped article according to claim 1 or 2, characterized in that the hydraulic binder comprises Portland cement and/or high alumina cement and/or high furnace cement and/or pozzuolana cement.

4. A shaped article according to any of claims 1 to 3, characterized in that the hydraulic binder comprises quartz as well as calcium hydroxide and/or cement.

5. A shaped article according to any of claims 1 to 4, characterized in that the mixture comprises as additive mica and/or vermiculite and/or perlite and/or pumice and/or coloring agents, as well as optionally bentonite, spiolite, amorphous silica, kaolin, wollastonite and ball clay.

6. A shaped article according to any of claims 1 to 5, characterized by the addition of polyelectrolytes, such as polyacrylamides and/or alkylsulfonates and/or alkylcellulose ethers.

7. A process for producing a shaped article according to any of claims 1 to 6, characterized in that or the mixture components in an arbitrary order or the dry mixture first obtained thereof are mixed with water in excess and in that the aqueous mixture, under simultaneous dewatering, such as during a Hatschek process, is undergoing a shaping operation.

8. A process according to claim 7, characterized in that the shaped article is undergoing, during the setting and/or thereafter, a water steam treatment at atmospheric pressure and/or a water-steam hardening at higher pressure and higher temperature.

Table 1

Data on breakage of the fibrocement plates manufactured according to example 1.

Essay according to DIN, average values of the longitudinal and transversal directions of the machine.

Later plate treatment (pressing)	Bending resistance N/mm^2	Breakage work kJ/m^2	Density g/cm^3	Water content %
Without pressing	18.4	1.605	1.353	31.2
180 bar 30 min	33.1	2.805	1.610	21.0

Table 2

Data on mechanical breakage of the fibrocement plates manufactured according to example 2.

Essay according to DIN, average values of the longitudinal and transversal directions of the machine.

Later plate treatment (pressing)	Bending resistance N/mm^2	Breakage work kJ/m^2	Density g/cm^3	Water content %
Without pressing	17.4	1.727	1.363	31.0
180 bar 30 min	32.0	2.605	1.524	22.1

Table 3

Data on mechanical breakage of the fibrocement plates pressed at 180 bar, 30 min, according to example 3.

Essay according to DIN, average values of the longitudinal and transversal directions of the machine.

Manufacture of the plates according to example N°	Birch cellulose fiber mixture (% by weight)	Linen cellulose fiber mixture (% by weight)	Sisal cellulose fiber mixture (% by weight)	Bending resistance N/mm^2	Breakage work kJ/m^2	Density g/cm^3	Water content %

1	20	70	--	26.3	1.955	1.495	23.8
1	40	50	--	28.8	2.483	1.500	23.3
1	60	30	--	31.0	2.602	1.502	23.6
1	80	10	--	32.8	2.945	1.504	23.4
2	20	--	70	33.1	3.568	1.531	22.9
2	40	--	50	33.0	3.251	1.540	22.7
2	60	--	30	32.9	3.375	1.539	22.8
2	80	--	10	33.4	3.105	1.537	22.8

Table 4

Data on mechanical breakage of the fibrocement plates pressed at 180 bar, 30 min, according to example 4.

Fiber concentration = constant = 6 % of unbleached birch cellulose to sulfate.

Manufacture of the plates according to example N°	Portland cement matrix (% by weight)	5000 Blaine quartz sand matrix (% by weight)	Perlite matrix (% by weigh t)	Mica matrix (% by weigh t)	Vermiculite matrix (% by weight)	Bending resistance N/mm^2	Breakage work kJ/m^2	Density g/cm^3	Water content %
1	800	--	200	--	--	29.5	2.453	1.427	27.5
1	700	--	300	--	--	27.5	2.115	1.348	29.0
1	800	--	--	200	--	28.4	2.382	1.542	25.7
1	800	--	--	--	200	26.9	2.004	1.492	26.9
2	600	400	--	--	--	32.4	2.614	1.553	22.0
2	540	360	100	--	--	28.4	2.210	1.380	26.5
2	540	360	--	100	--	30.0	1.050	1.405	26.0

Table 5

Data on mechanical breakage of the quartz sand and calcium hydroxide fiber plates, treated in autoclave, according to example 5, pressed at 180 bar, 30 min.

Fiber concentration = constant = 8 % of unbleached birch cellulose to sulfate.

Matrix = 92%		Bending resistance N/mm^2	Breakage work kJ/m^2	Density g/cm^3	Water content %
5500 Blaine quartz dust (parts by weight)	Calcium hydroxide (parts by weight)				
550	300	28.5	2.705	1.483	24.1
550	375	26.9	2.245	1.427	27.1
550	450	25.7	2.010	1.376	28.5

Table 6

Data on mechanical breakage of the fibrocement plates manufactured according to example 2, pressed at 180 bar, 30 min.

DIN essay, average values of the longitudinal and transversal directions of the machine.

Type of cellulose fibers	Fiber mixtures % by weight										
Birch	5	8	--	--	--	--	--	6	4	6	4
Eucalyptus	--	--	5	8	--	--	--	--	--	--	--
Pinus radiata	--	--	--	--	8	--	--	--	--	--	--
Sisal	--	--	--	--	--	8	--	2	4	--	--
Abaca	--	--	--	--	--	--	8	--	--	2	4
<u>Data on mechanical breakage</u>											
Bending resistance N/mm2	27.9	34.2	20.8	28.8	26.4	29.4	33.1	30.8	32.5	34.0	34.7
Breakage work kJ/m^2	1.004	2.884	0.727	1.474	1.775	3.680	4.101	3.405	3.248	3.002	3.163
Density g/cm^2	1.705	1.541	1.710	1.556	1.549	1.552	1.540	1.557	1.555	1.545	1.543
Water content %	20.3	22.8	20.1	22.0	22.2	22.7	23.0	22.4	21.9	22.9	22.8

Table 6a (properties of the materials)

8% by weight of cellulose / 55% by weight of cement / 37% by weight of quartz

	Fir tree cellulose	Eucalyptus cellulose	Birch cellulose
Bending resistance (N/mm^2)	14.2	21.3	24.7
Breakage power (kJ/m^2)	0.99	0.94	1.69
Apparent density (g/cm^3)	1.53	1.427	1.422
Water content (%)	32.3	33.1	27.1
Plate thickness (mm)	6.1	6.2	6.1

Average values of each one of 100 shaped plates (without pressing);

Direct molding machine corresponding to example 2; unbleached birch cellulose versus bleached eucalyptus and fir tree celluloses.

Table 7 (variants of mixtures for undulated plates)

	Mixture N°			
	1	2	3	4
Birch cellulose	8	6	6	--
Pinus radiata 65° SR	--	2	--	--
Abaca 65° SR	--	--	2	--
Eucalyptus	--	--	--	8
Ball clay	10	10	10	10
Quartz	27	27	27	27

Cement	55	55	55	55

Table 8

Characteristics of the undulated plates manufactured according to example 7 with the mixtures of table 7, essay according to DIN

Mixture N°	Bending resistance N/mm^2	Breakage power Nm	Density g/cm^3	Water content %
Non pressed				
1	19.8	67.3	1.527	24.0
2	18.2	78.8	1.519	24.2
3	21.9	92.4	1.517	24.1
4	16.8	52.1	1.529	23.9
Pressed				
1	27.2	105.4	1.820	15.3